

Weathering of granite surfaces – results from chemistry, Sr and S isotopes.

Peter Torssander¹, Carl-Magnus Mörrth¹, Ingunn Thorseth², and Göran Åberg³

¹Div. Environmental Isotope Geochemistry, Dept. of Geology and Geochemistry, Stockholm University, S-106 91 Stockholm Sweden. peter.torssander@geo.su.se

²Department of Geology, University of Bergen, Bergen, Norway.

³Department of Environmental Technology, Institute for Energy Technology, P.O.Box 40, N-2007 Kjeller, Norway.

Increased weathering rates of natural stone in buildings and cultural heritage have become an acute problem as a response to acid deposition. In Tanum, SW Sweden, there are numerous rock carvings of high preservation interest from the Swedish Bronze Age. During recent decades these rock carvings deteriorate, vanish and disappear at a high rate. The area is severely affected by acid rain, and the proximity to the North Sea exposes the rock surfaces to high salt concentrations and give the area a relatively mild climate. During winter snow covers are seldom stable and the temperature is often around the freezing point of water. These are the worst possible conditions for physical weathering which easily can overcome the chemical weathering that initializes the process.

Many ideas for the preservation of rock carvings have been and are currently applied in Scandinavia. These ideas include roof covered rock surfaces combined with water cleaning at known intervals and burial with different types of material such as soil, peat as well as artificial materials. The purpose of this intense chemical study is to determine the sources and sinks of elements so that the rock weathering rates can be calculated and determine whether a roof with occasional water cleaning could serve as protection technique. The weathering rates can later be used to evaluate different preserving techniques.

Methodological approach

Chemical weathering of the rock surface is one source for the elements found in runoff waters. The chemical weathering can be calculated with mass balances if other sources are identified and subtracted. To separate between the sources, throughfall, rain and bulk deposition are collected as measurement of the input, while runoff from the rock surface is collected from two small (about 2 m²) large confined ponds on the rock surface. Chemical analysis is made of all these waters for major- and trace elements and isotopes (Sr and S). The rock surface pond open to deposition (open pond) is sampled during rainfall, while the rock surface pond under roof (roof pond) was sampled during washing with 2L de-ionized water on a weekly basis 1998. The following year the roof pond was washed with the same amount deionized water as rock surface pond, that is, as the rainfall. One-m long drill cores (7 cm in diameter) were sampled during the roof construction in late 1997. The mineralogical composition of the rock was determined by visual inspection in hand-specimen and microscopic analyses.

In order to determine the weathering rate, it is necessary to have knowledge about the ponds' areas and water balance quite exactly and desirable to know the surface

temperature and time the surfaces stay wet. At an early stage in our investigation a computer-logged system equipped with a mobile telephone was installed at the site. The purpose was to ensure a continuous recording of temperature and relative humidity in the air and on the rock surfaces below and outside the roof, and similarly, continuous determination of rainfall and conductivity of runoff water. Data is logged every ten minutes and collected daily. An attempt is also made to determine the physical weathering through collection of rock fragments in the ponds and collection of small rock particles in filtered samples from the runoff. These are analysed mineralogically and chemically.

Results and Discussion

The granite rock has a rather heterogeneous modal composition of quartz, plagioclase, potassic feldspar and minor biotite. It has a typical chemistry for a granite with more than 70 % SiO₂ and rather high alkali concentrations (up to 7% K₂O). It has a weathered surface down to several (2-3) cm depth.

Comparisons of ICP-MS (HR) analysis between deposition and runoff samples show that the trace elements U, Nd, La, Ga, Ce, Mo, Pr, Sm, Sc, Sr, Ti, Y, and Zr are enriched in runoff. Other elements like N, S and Cl are enriched in the atmospheric deposition. Analyses of dissolved and particulate faces show that 0-50% of the trace elements are in particulate form. Blanks from de-ionized water show that the contribution to the trace element contents is less than 1%. There is a strong correlation between Na and Mg versus Cl in the water samples, indicating a large influence of the coastal proximity. In fact it has been problematic to use Na and Mg in the mass balance calculations.

Strontium isotope ratios (⁸⁷Sr/⁸⁶Sr) vary in the fresh rock minerals from around 0.72617 for fresh plagioclase (mean for more than 20 samples) and 0.821172 for K-feldspar (mean for 20 samples) and ⁸⁷Sr/⁸⁶Sr ratios for whole rock of around 0.7913. The average ⁸⁷Sr/⁸⁶Sr ratios in water from the rain collectors (0.70963) are very similar to the seawater Sr ratio, while bulk deposition (0.71032) and throughfall (0.71052) show slight increases of the ratio. The samples from the rock surface pond and the roof pond exhibit higher ⁸⁷Sr/⁸⁶Sr ratios: both ponds average at around 0.713 but interestingly, during the summer of 1998 the ⁸⁷Sr/⁸⁶Sr ratio in the rock surface was 0.7151 due to higher weathering input during the higher temperatures obtained at the open rock surface. Extremely good correlation is found between Ca and Sr, concurring that Sr isotope ratios appear to be a promising tool for the evaluation of weathering data, previously used in catchment studies (Åberg et al. 1989).

Highest δ³⁴S values in the deposition are found in throughfall, large variations occur in bulk deposition and the lowest δ³⁴S values are found in samples from the rain collectors. The runoff from the ponds has generally high S concentrations and variable δ³⁴S between +4‰ and +9‰. Basically, this indicates two sources of S: an anthropogenic source and sea salt, previously noted in the nearby located Lake Gårdsjön area (Torssander & Mörtz 1998).

ICP-MS analyses of the filters show that an important part of the weathering products are small rock fragments contributing to the total weathering rate. Chemical weathering rates have been estimated without correction for specific surface area. For the time period 1998-1999, the maximum chemical weathering rate (release rate of Si) varies between $1 \cdot 10^{-12}$ and $3 \cdot 10^{-16}$ mole/cm²/s with a mean of $2.2 \cdot 10^{-13}$ mole/cm²/s (the open pond), which is about 100 times faster than experimental data (Schweda 1990). The rate is positively correlated with the rock surface temperature. Also, the runoff pH from the pond under the roof varies between 5.5 and 6.5 while the pH in runoff from the pond outside the roof is between 4 and 5 similar to the atmospheric deposition. The rock surface under the roof has a mean maximum Si release rate of $3.5 \cdot 10^{-14}$ mole/cm²/s. In 1998, the roof pond weathering rate was more than 30 times slower (500 mm rainfall compared to 40 mm that is poured over the roof pond), while in 1999 the release rates were only some 3.5 times faster for the open pond (with equal amounts "rainfall"). This indicates that a roof does not inhibit weathering to an extent so that it can be used as a preservation technique.

The chemical release rate presented above can be expressed in terms of rate constants of the different minerals using the percentage of the mineral and the amount of released cations associated with the specific mineral. This calculation is done for calcium which originates from plagioclase weathering and the rate calculated for plagioclase weathering becomes $1 \cdot 10^{-13}$ mole fsp/cm²/s and $8 \cdot 10^{-14}$ mole fsp /cm²/s for the reference pond and the roof pond respectively. Using the BET surface area (only one small piece) gives a mean value for the reference surface, $4 \cdot 10^{-17}$ and for the roof pond $2 \cdot 10^{-17}$ mole fsp./cm²/s. Comparing these results with laboratory data at the same pH values as measured in the field and at 25°C, $3 \cdot 10^{-16}$ mole fsp./cm²/s¹, the rate are about 10 times slower in the field.

Conclusions

Trace elements, S- and Sr isotopes form a promising tool that could be used to evaluate weathering data. The results indicate that the release rate of Si from a granite rock surface could only be slightly reduced with the aid of a roof and cleaning of the rock surface with de-ionized water. As a consequence, a roof cover can hardly be used as a preservation technique for rock art.

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